Resonant Soft X-Ray Emission Spectroscopy of Vanadium Oxides and Sulfides

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INTRODUCTION

3d transition metal oxides display a broad variety of electronic, magnetic and structural material properties. Vanadium oxides show different electronic behavior depending on their valence configuration. The binary vanadium oxides V_2O_3 [1] (with a formal valence shell configuration of V $3d^2$) and VO_2 [1, 2] (formal configuration V $3d^1$) exhibit insulator-to-metal transitions at 160 K and 340 K, respectively. The ternary vanadium oxides NaV_2O_5 [3] and LiV_2O_4 [4] are particular interesting since they show extraordinary behavior. NaV_2O_5 is regarded to be the second example for an inorganic spin-Peierls (SP) [3] compound, showing many materials properties consistent with a SP-transition at 34 K. LiV_2O_4 is a conducting nonmagnetic metal down to the lowest temperatures and is known to be the first heavy fermion (HF) d-electron material [4]. The vanadium sulfide $BaVS_3$ [5] exhibits successive phase transitions, a structural transition ($\sim$ 240 K), a metal-to-insulator ($\sim$70 K), and an orbital ordering transition ($\sim$30 K).

The present work addresses the study of the electronic structure of these binary and ternary vanadium oxides and sulfides by the means of x-ray absorption spectroscopy (XAS) and resonant soft x-ray emission spectroscopy (resonant SXES). Resonant SXES is based on a two photon process and maps the occupied valence electron states. Core electrons excited by x-ray photons undergo a transition to an intermediate core-excited state. This intermediate state decays to a final valence excited state or the ground state via fluorescence of an x-ray photon.

EXPERMIMENTAL

The investigated binary vanadium oxide samples were single crystals (approximately 2 mm x 2 mm x 0.1 mm). The examined ternary NaV_2O_5 [3] was a single crystal as well, while LiV_2O_4 [4] and $BaVS_3$ [5] were polycrystalline powders. All experiments were performed at the undulator beam line 7.0.1 with a spherical-grating monochromator at the Advanced Light Source (ALS), Lawrence Berkeley Laboratory. The x-ray absorption spectra were measured by recording the total electron yield (TEY) and the fluorescence yield (FY) while scanning the photon energy of the incident monochromatized synchrotron radiation. TEY absorption spectra were recorded by measuring sample current and FY absorption spectra were measured with a channel electron multiplier. The XAS spectra were normalized to the photo current from a clean gold mesh introduced into the synchrotron radiation beam in order to correct for intensity variations of the incident x-ray beam. The soft x-ray fluorescence was recorded with a high-resolution Rowland-mount grazing-incidence grating spectrometer [6] with a two-dimensional detector.

RESULTS AND DISCUSSION

The upper part of Fig. 1 displays the XAS spectra of V_2O_3 [1] in TEY and FY mode recorded with a monochromator energy band pass of approximately 0.2 eV. Between 510 eV and 527 eV the V L-spectra are split into the approximately 7 eV separated spin-orbit doublet.
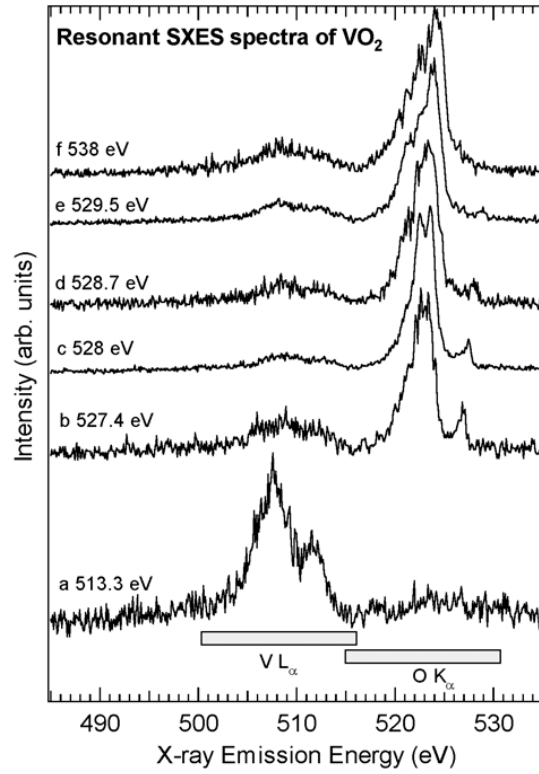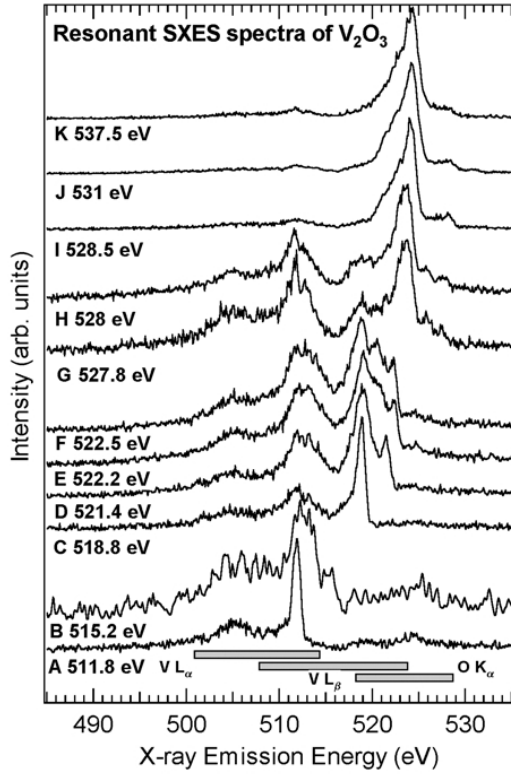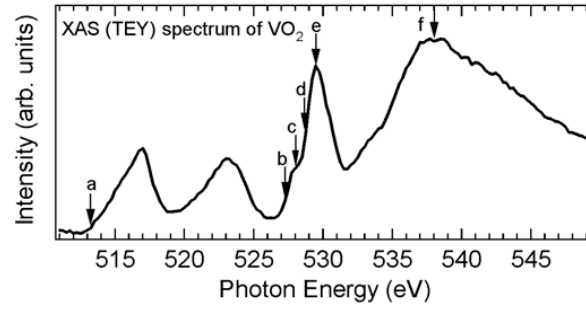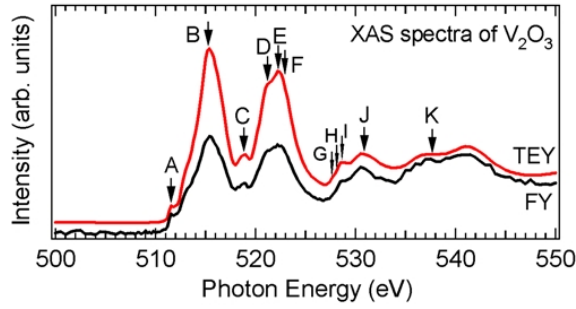
Figure 1. V L and O K x-ray absorption spectra (upper part) of V_2O_3. Resonant soft x-ray emission spectra (lower part) of V_2O_3.

Figure 2. V L and O K x-ray absorption spectra (upper part) of VO_2. Resonant soft x-ray emission spectra (lower part) of VO_2.

The absorption band from 510 to 518 eV corresponds to the V $2p_{3/2} \rightarrow$ V 3d transition (V L_3) and the one from 518 to 527 eV to the V $2p_{1/2} \rightarrow$ V 3d transition (V L_2). Just above the V L_2-edge (527 eV) the O K-edge is found. The double-peaked part of the XAS spectrum centered around 530 eV (527 – 533 eV) is attributed to O 2p states hybridized with unoccupied crystal field split V 3d states. The structure around 541 eV is interpreted according to a hybridization of O 2p states with V 4sp states. Note that the absorption spectra taken in TEY and FY mode behave similar besides a reduced intensity of the V L-bands in the FY mode spectrum relative to the O K-band. Therefore it was reasonable to choose the proper excitation energies for the resonant SXES according the TEY spectrum, being recorded with higher statistics.

The lower part of Fig. 1 shows the resonant SXES spectra excited with a band pass of ca. 0.2 eV at the energies marked by the arrows in the XAS spectrum above. The V L_α-band (3d4s $\rightarrow 2p_{3/2}$) and the V L_β-band (3d4s $\rightarrow 2p_{1/2}$) are centered at 512 eV and 519 eV, respectively, and have considerable overlap. Above these V L-emission bands (see the marked regions at the energy scale of Fig. 1) the O K_α-emission band is spread around 524 eV. The overlap of the V L_β-band

with the O K_α-band is again visualized with marked energy regions at the energy scale of the emission spectra. By resonant excitation we can tune the energy to the V $2p_{3/2}$ threshold thereby eliminating this overlap. Thus the bottom spectrum of Fig. 1 can be considered as the V 3d projected density-of-states (DOS) of V_2O_3. Resonant inelastic x-ray scattering (RIXS) is weak due to the metallic character of V_2O_3 at room temperature. Nevertheless, in spectrum E – K we see energy loss features which we attribute to V-dd excitations on the high energy sides of the V L_β- and O K_α-emission band, respectively. The top 3 spectra are dominated by the O K_α - emission. Here the O 2p character of the valence band is reflected.

The XAS spectrum of VO_2 recorded in TEY mode displayed in the upper graph in Fig. 2 is similar in energy positions of the absorption bands as the V_2O_3 XAS spectrum. In the lower graph of Fig. 2 resonant SXES spectra are displayed excited with the energies marked with arrows in the VO_2 XAS spectrum above. The energy dependence of the O K_α-emission band is thought to be due to RIXS features and different oxygen sites.

Distinct RIXS features are seen in the resonant SXES spectra of the around room temperature insulating NaV_2O_5 (not shown here). This contradicts to the V_2O_3 (at room temperature metallic) showing just very weak RIXS. LiV_2O_4 shows strong excitation energy dependence in the resonant SXES spectra of the O K_α- emission band. This energy dependence is explained by the successive excitation of different orbitals. By applying resonant SXES spectroscopy to $BaVS_3$ the S 3s- and S 3d-DOS were studied. It is planned for the future to record resonant SXES when cooling $BaVS_3$ and the here investigated vanadium oxides to their low temperature phases by the use of a cryostat.

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